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09/996,244	11/28/2001	Daniel Richard Schaefer	594826-001	3771
27805 7590 08/29/2008 THOMPSON HINE L.L.P. Intellectual Property Group P.O. BOX 8801 DAYTON, OH 45401-8801			EXAMINER PALABRICA, RICARDO J	
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**Please find below and/or attached an Office communication concerning this application or proceeding.**

The time period for reply, if any, is set in the attached communication.

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BEFORE THE BOARD OF PATENT APPEALS  
AND INTERFERENCES

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Ex parte DANIEL RICHARD,  
AND JAMES MICHAEL SNEAD

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Application No. 09/996,244  
Technology Center 3600

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Mailed: August 29, 2008

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Before DALE M. SHAW *Chief Appeals Administrator*.  
SHAW, *Chief Appeals Administrator*.

This application was received electronically at the Board of Patent Appeals and Interferences on April 9, 2008. A review of the application has revealed that the application is not ready for docketing as an appeal. Accordingly, the application is herewith being returned to the examiner. The matter requiring attention prior to docketing is identified below:

Application No. 09/996,244

On September 27, 2007, an Examiner's Answer was entered into the record. On page 3 of the Examiner's Answer, the examiner cites "Jimenez-Vazquez, "Hot-atom incorporation of tritium atoms into fullerenes, 'Chemical Physics Letters," 21 October 1994, pp. 111-114" and Bolz et al. "CRC Handbook of Tables for Applied Engineering Science, published by the Chemical Rubber Co., p. 390 (1970)" as prior art. However, copies of the references are missing from the electronic file.

Accordingly, it is

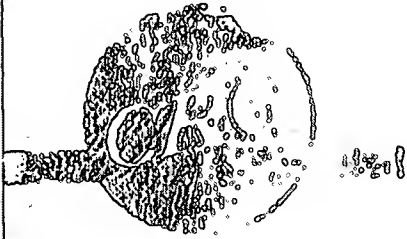
**ORDERED** that the application is returned to the Examiner:

- 1) to enter the missing references into the electronic file; and
- 2) for such further action as may be appropriate.

If there are any questions pertaining to this Order, please contact the Board of Patent Appeals and Interferences at 571-272-9797.

DMS/dal

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of.

Table 4-51. PORTABLE RADIATION-DETECTING DEVICES\*

ROBERT RADTKE

See also Section 9.2.

## ABBREVIATIONS AND SYMBOLS:

 $c/m$  = counts per minute $m/hr$  = milliroentgen per hour $n_f$  = fast neutron $n_{th}$  = thermal neutron $R/hr$  = roentgen per hour

Detector	Radiation detected	Range <sup>b</sup>	Uses	Comments
Geiger-Mueller (G-M) tube	Alpha Beta X Gamma	0.04 m/hr to 500 m/hr	Low dose-rate surveys Area monitors Personnel radiation monitors	1. Radiation detected depends on type of G-M tube 2. Energy dependent 3. Some models saturate - do not use in high radiation fields 4. Sensitive to microwave fields 5. Ratemeter and audible pulse 6. Rapid response 7. Rugged, dependable
Ion chamber	Alpha Beta X Gamma	3 m/hr to 10,000 R/hr	Medium and high dose-rate surveys Area monitors	1. Wide dose-rate range on a single instrument 2. Low energy dependence 3. Some models can be used in RF fields 4. Some models slow to respond
Scintillation	Alpha Beta X Gamma Neutrons	0.025 m/hr to 200 m/hr or to 500,000 c/m	Low-level contamination surveys	1. High sensitivity 2. Rapid response 3. Fragile 4. Audible signal and ratemeter 5. Radiation detected depends on instrument and crystal 6. Fast neutron detector where dose rate is not required
Proportional counter	Alpha Beta X Gamma Neutrons	to 500,000 c/m  to 20,000 $n_{th}/cm^2/sec$ to 100 m/hr/hr $n_f$	Low-level contamination surveys Neutron survey	1. Primary use is for alpha detection or neutron surveys 2. Alpha detector can discriminate between alpha and beta-gamma 3. Neutron detector can discriminate against gamma radiation 4. Maintenance may be a problem
$BF_3$ counter	Neutrons	to 100,000 c/m	Survey	1. Rather low sensitivity 2. Bulky 3. Used with various moderators

\*From "CRC Handbook of Radioactive Sources", Y. Wang, Ed., The Chemical Rubber Co., 1960.

## REFERENCE

For further information on rate-measuring instruments (then detectors, selection, maintenance, and calibration), see "Radiation Accidents and Emergencies" L. H. Lanzl, J. H. Pingle, and J. H. Rust, Eds., Charles C. Thomas, 1965.

## Hot-atom incorporation of tritium atoms into fullerenes

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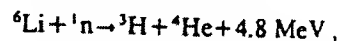
### Abstract

We have used classical hot-atom chemistry to put tritium atoms inside fullerene molecules. The tritium is generated in a nuclear reactor with the reaction  ${}^6\text{Li}(n, \alpha){}^3\text{H}$ . The hot tritium atom slows down and can end up being thermalized inside a fullerene where it is trapped. The irradiated sample is dissolved, chromatographed, and counted in a scintillation counter, showing a small tritium activity. After some time, the sample is analyzed with a sensitive mass spectrometer, and  ${}^3\text{He}$  was found on heating above 400°C, showing that the tritium had decayed leaving the  ${}^3\text{He}$  trapped inside the fullerene.

The fullerenes are closed 'cages' [1] with cavities large enough to contain atoms. Groups at Rice [1-3] and IBM [4,5] have been able to generate small amounts of metal-containing fullerenes although it has been extremely difficult to separate and isolate pure substances. Schwarz and co-workers [6-8], and others [9], have reported the generation of  $\text{He}@C_{60}$  through collision of  $C_{60}^+$  with helium, in a mass spectrometer. No material could be isolated in these experiments. We have recently reported [10-12] that it is possible to introduce the noble gases, He, Ne, Ar, Kr, and Xe into both  $C_{60}$  and  $C_{70}$  by heating them at around 600°C in an atmosphere of the corresponding gas. Hundreds of milligrams of material were obtained with noble gas atoms incorporated in about one out of a thousand molecules. This method is unlikely to incorporate tritium atoms into fullerenes, since it would be difficult to produce tritium atoms at the same time as bonds are broken in the fullerene to admit them to the inside.

An alternative is hot-atom chemistry [13]. An atom is generated at high energies by a nuclear reaction. It loses energy by ionizing molecules and by

breaking bonds. Before it becomes fully thermalized, it can react at energies of several electron volt to form stable molecules by way of reactions that are thermally impossible. If the atom is radioactive, it can be detected in extremely small amounts. We chose tritium ( ${}^3\text{H}$ ) because it can be made easily, has a convenient half life (12.3 yr), and is easy to handle and detect. Tritium is generated at an energy of 2.7 MeV by the nuclear reaction



where  $n$  is a thermal neutron. The products have high kinetic energy, but will rapidly lose it in condensed media ultimately passing through the energy range where some of the  ${}^4\text{He}$  and  ${}^3\text{H}$ -produced could penetrate fullerene molecules and be trapped. We therefore needed to prepare a sample containing Li and fullerenes, and expose it to neutron irradiation.

We prepared a lithium salt of the fullerenes to ensure intimate contact between the lithium atoms (ions) and the fullerene molecules. One very important consideration in planning the experiment is to limit the radiation damage to the sample. If the total

amount of energy released (4.8 MeV/T) exceeds about 1 eV/fullerene molecule, all the fullerene will be destroyed. This means that the amount of lithium, the irradiation time, and the neutron flux must be carefully controlled. We used the commercial mixture of  $C_{60}/C_{70}$ , provided by either Aldrich or Texas Fullerenes. Two methods of making the lithium salt were tried. We first made the hexalithium salt as described by Olah and co-workers [14]. They used a large excess of lithium. The fullerene polyanions were generated by sonicating 20 mg of Li with 20 mg of fullerenes (a 100-fold molar excess) in dry tetrahydrofuran (THF). The  $Li_6C_{60}$  salt dissolves in the THF. The solution is filtered, transferred to the silica irradiation ampoule. The solvent is then removed, the ampoule is then evacuated and sealed off. The reaction is difficult because it requires three phases, since neither Li nor fullerenes dissolve in THF. The whole operation must be done in a dry box in the absence of oxygen and water. We then tried the dilithium salt. We started by making the radical-anion of naphthalene in dry THF using one equivalent of lithium, one equivalent of naphthalene, and sonication. After the lithium naphthalenide was ready, the solution was transferred to another flask containing 0.1 equivalents of the fullerene mixture dissolved in an equal volume of dry benzene. All of this was done under inert (Ar) atmosphere. The solution was slowly transferred to a fused silica tube, where the solvent was evaporated using heat and a constant flow of argon. After all the solvent was gone, the tube was evacuated for several hours using a diffusion pump, in order to remove as much naphthalene as possible.

The ampoule was made of fused silica in order to avoid exposure of atoms other than Si, O, C, and Li to the neutrons. This prevents the formation of other radioactive isotopes. Pyrex contains both Na and B which absorb neutrons. The samples were sent to the Brookhaven National Laboratory, where they were irradiated in the Medical Reactor for 30 s with a low neutron flux of  $1.5 \times 10^{12}$  n/cm<sup>2</sup> s. Most reactors have a flux which is more than sufficient to destroy the sample in the minimum practical irradiation time. After irradiation, the ampoules were opened and the contents neutralized with aqueous acid. The material was then extracted with toluene and purified by chromatography using a column of neutral alumina. A large fraction of the sample was insoluble in both

water and toluene. This insoluble tar was presumed to be a polymer of fullerene formed by radiation damage. Indeed, in the first two samples that we irradiated, we naively assumed that fullerenes were robust and would tolerate a large amount of radiation. The entire sample was insoluble tar. The chromatographed samples were then counted in a liquid scintillation counter using Opti-Fluor as the scintillation cocktail. Although the activity was a few times the background level, it persisted after the sample was refluxed in water and toluene.

This result supports the hypothesis that tritium is strongly bound to the fullerene. However, it does not prove that the tritium is inside the fullerene molecule. Tritium could form a bond to the outside of the fullerene. How could this possibility be excluded? If the tritium were bound to the outside of  $C_{60}$ , the  $^3He$  generated by its radioactive decay would be lost. However, if the tritium were inside, the  $^3He$  would be trapped, since almost all of the energy released in the  $\beta$  decay goes into the electron and the antineutrino. Furthermore, if most or all of it were inside the number of helium atoms formed could be predicted from the decay of the tritium during the time the sample was stored. A comparison between the estimated and the observed amount of  $^3He$  would then reveal where in the fullerene the tritium was.

The sample was stored for 15 months, after which it was once again chromatographed, because we noticed that some of the sample had developed insoluble material. This time, however we carried out the chromatography using norite-A and toluene [15]. A solution (0.25 ml) of this material ( $C_{60}$ ) with a concentration of  $2.1 \times 10^{-4}$  g/ml had a tritium activity of 35 counts per minute (cpm) including a background count of 23 cpm. The efficiency of the scintillation counter was estimated to be around 58% by measuring the activity of a tritium standard. The number of disintegrations per minute (dpm) for the material was therefore 390 dpm/mg. The original activity of  $C_{60}$  at the time of irradiation was 420 dpm/mg. The number of tritium atoms that decayed over 15 months is  $2.7 \times 10^8$  atoms/mg of sample.

We also analyzed a sample of 0.57 mg of the material for  $^3He$  using mass spectrometry as described in our previous paper [10]. The tritium-doped  $C_{60}$  was heated in steps, and the total amount of  $^3He$  released was measured, see Table 1. The amount of  $^3He$

Table I  
Release of  $^3\text{He}$ 

Time (min)	Temp (°C)	$^3\text{He}$ ( $10^{-13}$ cc/mg)	$^4\text{He}$ ( $10^{-12}$ cc/mg)	$^{22}\text{Ne}$ ( $10^{-12}$ cc/mg)	$R^a$
60	220	735	870	210	1.3
60	400	2751	2630	193	4.4
80	550	1886	2280	140	5.2
90	700	2509	40175	123	105

<sup>a</sup>  $R$  is the ratio of  $^4\text{He}$  to  $^{22}\text{Ne}$  divided by the ratio found in air.

roughly three orders of magnitude above background. As we showed previously [10], fullerenes, made in an arc with a low pressure of helium, contain small amounts of  $^4\text{He}$ . The amount seen here,  $4.8 \times 10^{-8}$  cm<sup>3</sup>/mg, is comparable to the amount found previously,  $3.5 \times 10^{-8}$  cm<sup>3</sup>/mg. The Ne is evidently an atmospheric contaminant and is on the outside of the fullerene, since it comes off at low temperatures. At low temperatures the ratio of  $^4\text{He}/^{22}\text{Ne}$  is comparable to that found in air. Each milligram of this material contained a total of  $7.9 \times 10^{-12}$  cm<sup>3</sup> of  $^3\text{He}$  (at STP). Therefore, each milligram of the material contained  $3.2 \times 10^{-16}$  mol of  $^3\text{He}$  or  $1.9 \times 10^8$  atoms of  $^3\text{He}$ . This is within 30% of the amount expected considering the radioactivity measurement and the storage time. Roughly one molecule in  $4 \times 10^9$  contains a tritium atom.

The fact that the two numbers are similar, strongly suggests that there is indeed tritium incorporated inside the  $\text{C}_{60}$ , and that, when it decays, the  $^3\text{He}$  atom remains trapped in the inside. There are several reasons for the disagreement between the two numbers. We do not know how much the  $\text{C}_{60}$  cage can shield the emission of a  $\beta$  particle. The scintillation fluid that we used for our samples was not the same as that used in the tritium standard, making it difficult to obtain a good efficiency factor for the scintillation counter. Finally, as the tritium decays, some of the  $^3\text{He}$  atoms might have enough energy to escape from the  $\text{C}_{60}$  cage.

We attempted to repeat the mass spectrometric analysis using another aliquot of the sample. During the time between preparing these aliquots we were engaged in preparing heavily labeled samples of fullerenes with up to 0.2% of  $^3\text{He}$  inside [11,12]. The first tritium-labeled sample was prepared before we were making fullerenes labeled with  $^3\text{He}$ . The second aliquot showed a hundred times the amount of  $^3\text{He}$

as the first. It had evidently become contaminated during preparation. At an incorporation level of 0.2% only  $7 \times 10^{-15}$  g of  $\text{C}_{60}$  is required to give the minimum sensitivity of  $10^4$  atoms of  $^3\text{He}$  and  $6 \times 10^{-11}$  g is equivalent to the entire first aliquot.

One can further speculate on the state of the tritium inside  $\text{C}_{60}$ . If the  $^3\text{H}$  atom enters a  $\text{C}_{60}$  molecule and binds to one of the carbon atoms, then the molecule is a radical which can react with other molecules, including fullerenes. This might account for some of the decomposition products, which might be some form of polymer. If the radical abstracts a hydrogen atom, a dihydro product is formed. However, this second process must occur outside the cage. Such a dihydro compound might chromatograph along with  $\text{C}_{60}$ , at least at low resolution. One might expect that the external hydrogen might be removed in strong base to produce an anion. The formation of the C-T and C-H bonds destroys two aromatic rings and severely puckers the surface of the fullerene. Both of these effects cost an appreciable amount of energy. Another possibility is that the tritium is unbound, simply trapped as an atom inside the fullerene cage. The species would be a free radical but might be unreactive.

We are grateful to the National Science Foundation for supporting this research under grants CHE-9023579, CHE-9204343, and CHE-931243. We are grateful to Professor François Diederich for supplying us with our first sample of fullerenes for this experiment.



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